The yield was 10% as determined by glpc. Several other unidentified substances were present in very small amounts.

Subjection of the brown semisolid to chromatography on a 10 × 1 in. column of alumina using hexane as the eluting solvent and adding benzene as the chromatography proceeded produced 0.29 g (50%) of 2,2′-azoxynaphthalene: mp 163° (lit.[30] mp 164°); nmr ($CDCl_3$) δ 7.2–8.2 (aromatic); ir (KBr) 1475 cm^{-1} (N=NO).

Reaction of *N*-(2-Biphenyl)hydroxylamine (11) with Hydrogen Fluoride. Freshly prepared **11** (1.82 g, 9.8 mmol) was slowly added to 100 ml of freshly condensed hydrogen fluoride at −60°. The mixture initially showed a blue color which changed to black after standing for several hours. After evaporation of the hydrogen fluoride, water (30 ml) and ether (30 ml) were added and the contents were neutralized with ammonia gas. The mixture was filtered to give a dark brown residue. The residue was shown to be carbazole (**23**) by comparison of its mass spectrum, infrared spectrum, and thin layer chromatography (silica gel) R_f data with those of an authentic sample of carbazole. The crude yield was 0.25 g (15%).

The filtrate was extracted with ether. The separated organic mixture was dried ($MgSO_4$) and concentrated on a rotary evaporator to give a brown oil. Chromatography on a 10 × 1 in. column of alumina using 1:1 benzene–hexane produced 1.0 g (60%) of 2,2′-azoxybiphenyl: mp 156° (lit.[31] mp 158°); nmr ($CDCl_3$) δ 7.2–7.5 (aromatic); ir (KBr) 1480 cm^{-1} (N=NO). These spectra were identical with those of authentic material.

A second eluent was obtained as a semisolid. It was identified as 5-fluoro-2-aminobiphenyl by comparison with an authentic sample.[32] The crude yield was 0.37 g (20%): mp 55–65; nmr ($CDCl_3$) δ 3.5–3.7 (broad, 2 H, NH_2) and 6.7–7.6 (m, 8 H, aromatic); ir (KBr) 3400, 3380 (NH_2), 830, 750 cm^{-1} (aromatic).

Reaction of *N*-(2-Biphenyl)hydroxylamine (11) with Sulfuric Acid. A mixture of 0.1 g (0.5 mmol) of **11** and 2 ml of 20% sulfuric acid was stored at room temperature for 1 hr. The resulting green mixture was extracted with chloroform. The dried ($MgSO_4$) chloroform solution was concentrated to give a dark green residue. Thin layer chromatography and mass spectral analysis (*m/e* 167, parent) were identical with those of authentic carbazole. The yield was 10%.

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Registry No.—Hydrogen fluoride, 7664-39-3.

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Synthesis of Cyclopropylmethanol Derivatives Bearing Electronegative Substituents[1a]

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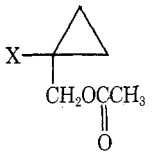
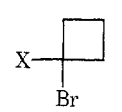
In this note we report a convenient synthesis of cyclopropylmethanol acetates bearing electron-withdrawing substituents at the 1 position. The data base for cyclopropylcarbinyl cation chemistry, for example, is provided in overwhelming part by experiments performed on carbon skeletons carrying electron-donating substituents.[2] Recent studies in the bicyclo[2.2.1]heptyl system have highlighted some interesting effects of electronegative substituents on the chemistry of the 2-cation.[3] Thus, one rationale for exploring synthetic approaches to electronegatively substituted cyclopropylcarbinyl derivatives lies in the proposition that such compounds should be of interest in the further elucidation of the chemistry of cyclopropylcarbinyl reactive intermediates.

The starting materials for the preparations of **1** were the known cyclobutyl derivatives **2** and conversions into **1**

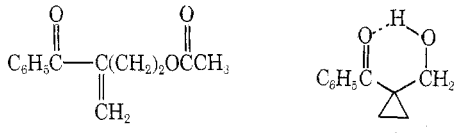


1a, X = COC_6H_5
b, X = CO_2CH_3
c, X = $CONH_2$
d, X = NO_2



2a, X = COC_6H_5
b, X = CO_2CH_3
c, X = $CONH_2$
d, X = NO_2
e, X = NO

were accomplished by heating each starting material in glacial acetic acid containing an excess of silver acetate.



3 4

In the case of **2a**, such treatment afforded a 65% yield of **1a** accompanied by its homoallylic partner **3** in a 3.4:1 ratio as determined by vpc and nmr spectroscopy. That ring contraction of **2a** had occurred was clearly seen from the nmr spectrum of the mixture which showed the typical AA'BB' pattern of a gem-disubstituted cyclopropane straddling δ 1.13 and a methylene singlet at δ 4.28. The isomers could not be cleanly separated by either spinning band distillation or by preparative vpc, and the structure of **3** was deduced from its nmr signals seen in the mixture of **1a** and **3**. Since **1a** was stable to reaction conditions, **3** must be a primary reaction product. Saponification of the mixture followed by alumina chromatography, however, afforded pure, crystalline hydroxy ketone **4** in 40% yield. In addition to its nmr and ir (CCl_4 3460 cm^{-1}, intramolecularly H bonded OH) spectra, the mass spectrum of **4** corroborated its structural assignment showing a strong M − 1 peak at m/e 175, characteristic of primary alcohols.[4]

The rearrangement of **2a** using silver oxide in dioxane–water and with mercuric acetate in acetic acid was briefly investigated. The former reagent yielded, after column chromatography, a noncrystalline mixture of **4** and an unknown compound in a ratio (vpc) of 1.7:1. The mercuric acetate reaction, which bears further investigation, yielded, by vpc, **1a**, starting material, **2a**, and a shorter-retention-time component, in roughly equal amounts. Interestingly, ketoacetate **3** was not among the volatile products of this reaction.

The rearrangement of bromo ester **2b** afforded **1b** and its homoallylic isomer in a 7:1 ratio. Fractionation gave 44% of **1b** contaminated by less than 4% of its isomer. Likewise, rearrangement of bromoamide **2c** gave pure, crystalline **1c** in 43% yield. In this instance the crude reaction mixture was not investigated for the presence of a homoallylic isomer.

The generality of the synthetic method was further illustrated by the conversion of **2d** into **1d** in 45% yield by using a sealed system at 210°. In an attempt to prepare the nitroso analog of nitrocyclopropane **1d**, the known nitrosoalkane **2e** was treated with acetic acid–silver acetate at 180–210°. The product of this reaction was, however, **1d** (plus some metallic silver).

Experimental Section

Nmr spectra were obtained on a Varian A-60A spectrometer[5] with tetramethylsilane internal standard. Ir spectra were obtained on a Perkin-Elmer 337 grating spectrometer and melting points (uncorrected) on a Thomas-Hoover melting point apparatus (Arthur H. Thomas Co., Philadelphia, Pa.). Vpc columns used were analytical, ⅛ in. × 6 ft 10% UC-W98 (Hewlett-Packard) on Chromosorb W, and preparative, ¼ in. × 6 ft 25% UC-W98 on Chromosorb W unless otherwise noted. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

1-Acetoxymethylcyclopropyl Phenyl Ketone (1a). A solution of 15 g (0.063 mol) of bromo ketone **2a**[6] in 200 ml of glacial acetic acid containing 11.46 g (0.068 mol) of silver acetate was refluxed 4 hr (optimum time). After cooling, the mixture was filtered and treated with charcoal and the solvent was evaporated *in vacuo*. The remaining oil was dissolved in 25 ml of ether, carefully washed with saturated $NaHCO_3$ and water, dried, and fractionated (20 cm Vigreux) to yield 9.07 g (65%) of **1a** and **3**, bp 126–129° (0.52 mm); vpc (180°) showed two peaks, **3** trailing **1a** with a relative retention time of 1.1; ir (smear) 3060 (aryl H), 1745 (ester C=O), 1675 cm^{-1} (ketone C=O); nmr (CCl_4) of **1a** δ 0.97 (2 H, m, cyclopropyl *trans* to benzoyl), 1.27 (2 H, m, cyclopropyl cis to benzoyl), 1.84 (3 H, s, acetate CH_3), 4.28 (2 H, s, CH_2OAc), 7.3–7.9 (5 H, m, typical benzoyl pattern); nmr of **3** δ 1.91 (s, acetate CH_3), 2.75 (broadened t, J = 6.5 Hz, C=CCH_2–), 4.19 (t, J = 6.5 Hz, CH_2OAc), 5.62 (broadened s, vinyl H trans to benzoyl), 5.87 (broadened s, vinyl H cis to benzoyl). Spinning band distillation (100°, 0.15 mm) effected concentration but not separation of **1a**. The close retention times on a variety of columns precluded large-scale preparative vpc.

1-Hydroxymethylenecyclopropyl Phenyl Ketone (4). A solution of 2.1 g (0.0096 mol) of a mixture **1a** and **3** and 2 equiv of 1 *N* NaOH in 50 ml of methanol was refluxed 1 hr on a steam bath. The mixture was diluted with saturated NaCl solution and extracted with $CHCl_3$ and ether. After drying ($MgSO_4$) and evaporation the crude product was dissolved in benzene and chromatographed over 50 g of alumina. The eluting solvents were petroleum ether, benzene, ether, and methanol. Fractions eluted with 25% ether in benzene up to pure ether contained **4**. These were combined and the product was crystallized by the addition of ether–hexane yielding 0.74 g (44%) of **4**, mp 54–58°. A portion was recrystallized from ether–hexane for analysis: mp 57–58°; ir (CCl_4) 3450 (broad, did not change on dilution, H bonded OH), 3050 (aryl H), 1675 cm^{-1} (C=O); nmr (CCl_4) δ 0.96 (2 H, m, cyclopropyl trans to benzoyl), 1.09 (2 H, m, cyclopropyl cis to benzoyl), 3.02 (1 H, broad s, OH), 3.67 (2 H, s, CH_2O–), 7.2–7.8 (5 H, m, typical benzoyl); mass spectrum (70 ev) m/e (rel intensity) 176 (9), 175 (31), 158 (12), 105 (100), 77 (70), 51 (24).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.82. Found: C, 74.82; H, 6.83.

Methyl 1-Acetoxymethylcyclopropanecarboxylate (1b). A solution of 7.2 g (0.039 mol) of bromo ester **2b**[7] in 60 ml of glacial acetic acid and a 10 mol % excess of silver acetate were refluxed for 4 hr. After cooling and filtration, the reaction mixture was poured carefully into cooled, saturated $NaHCO_3$ solution which was then extracted thoroughly with ether and $CHCl_3$. Drying and evaporation yielded a crude product, the nmr of which indicated the presence of 12% of a homoallylic isomer of **1b** (signals at δ 5.60 and 6.19 for vinyl H). Fractionation (20 cm Vigreux) yielded 3.0 g (44%) of colorless **1b**: bp 103–104° (12 mm); $n^{24.5}D$ 1.4415; ir (smear) 1730 (broad, ester C=O's); nmr (CCl_4) δ 0.93 (2 H, m, cyclopropyl trans to carbomethoxy), 1.24 (2 H, m, cyclopropyl cis to carbomethoxy), 2.00 (3 H, s, acetate CH_3), 3.68 (3 H, s, OCH_3), 4.15 (2 H, s, CH_2OAc).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03; O, 37.17. Found: C, 55.61; H, 7.03; O, 36.89.

1-Acetoxymethylcyclopropanecarboxamide (1c). A solution of 0.35 g (0.0019 mol) of bromoamide **2c**[7] in 10 ml of glacial acetic acid with 10 mol % excess of silver acetate were refluxed 4 hr. Work-up as with **1a** (charcoal omitted, $CHCl_3$ used to extract) afforded an oil which crystallized on addition of ether yielding 0.13 g (43%) of **1c**, mp 94–95°. Recrystallization from ether (large amount) gave an analytical sample (same mp): ir (KBr) 3445 (NH, free), 3150 (NH, assoc), 1725 (ester C=O), 1680 (amide C=O), and 1625 cm^{-1} (NH_2); nmr ($CDCl_3$) δ 0.91 (2 H, m, cyclopropyl trans to carbamoyl), 1.33 (2 H, s, m, cyclopropyl cis to carbamoyl), 2.15 (3 H, s, acetate CH_3), 4.28 (2 H, s, CH_2OAc), 6.62 (2 H, very broad s, NH_2).

Anal. Calcd for $C_7H_{11}NO_3$: C, 53.49; H, 7.05; N, 8.91. Found: C, 53.62; H, 7.05; N, 8.62.

1-Acetoxymethyl-1-nitrocyclopropane (1d). A mixture of 1.00 g (5.4 mmol) of **2d**,[8] 1.55 g (9.3 mmol) of silver acetate, and 60 ml of glacial acetic acid were sealed under nitrogen in a Pyrex tube which, in turn, was heated in an autoclave at 210° for 20 hr. The reaction mixture was diluted with 200 ml of water and neutralized with solid $NaHCO_3$. Extraction of the aqueous portion with 3 × 100 ml of methylene chloride, drying (Na_2SO_4), and distillation of the solvent gave a crude product which was further purified by chromatography (silica gel, ether–pentane eluent) to give 0.39 g (45%) of product, which for practical purposes, was pure (vpc, 15% Carbowax on Chromosorb W). Molecular distillation [bp 63° (0.2 mm)] gave an analytical sample: ir (neat) 1760 (C=O), 1550 and 1300 (NO_2) cm^{-1}; uv max (C_2H_5OH) λ 205 nm (ϵ 9900); nmr ($CDCl_3$) δ 1.3 and 1.9 (2 H each, A_2B_2 m, cyclopropyl H's trans and cis to NO_2, respectively), 2.06 (3 H, s, acetoxy CH_3), 4.58 (2 H, s, CH_2).

Anal. Calcd for $C_6H_9NO_4$: C, 45.28; H, 5.70; N, 8.80. Found: C, 44.99; H, 5.75; N, 9.09.

Registry No.—**1a**, 51175-74-7; **1b**, 51175-75-8; **1c**, 51175-76-9; **1d**, 51175-77-0; **2a**, 51175-78-1; **2b**, 51175-79-2; **2c**, 51175-80-5; **2d**, 51175-81-6; **3**, 51175-82-7; **4**, 51175-83-8.

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Synthetic Reactions by Complex Catalysts. XXXIII. Synthesis of Vinylcyclopropane Derivatives by Copper Isonitrile Complexes. Copper Vinylcarbenoid Intermediates

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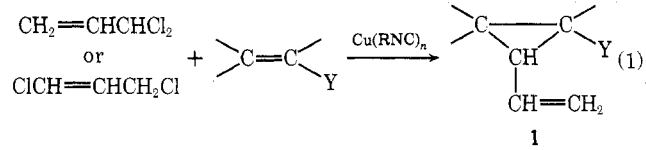
Several attempts[1] to prepare vinylcyclopropanes by means of vinylcarbenes generated from the corresponding diazo compounds and metal carbenoids have been made. Most of those attempts, however, have not given satisfactory results, because vinylcarbenes readily undergo intramolecular cyclization, leading to preferential formation of cyclopropenes.

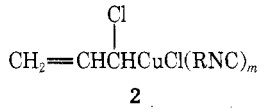
Herein, we present a new and facile synthesis of vinylcyclopropane derivatives (**1**), utilizing copper carbenoid-isonitrile intermediates (**2**) which are formed by the reaction of allylidene dichloride or 1,3-dichloropropene with a Cu(0)-isonitrile complex (eq 1).



(1)

1

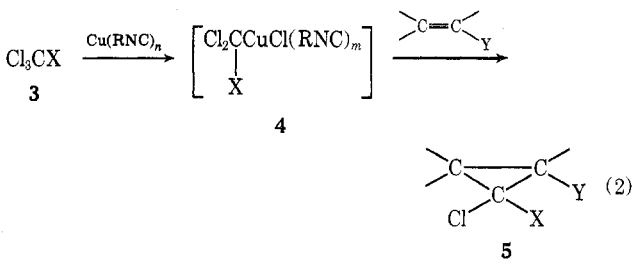
Y = CO_2R



2

In previous papers[2] we reported a synthetic method of cyclopropane ring formation in which a mixture of metallic copper and isonitrile was treated under nitrogen with a polyhalomethane derivative (**3**) to produce an organocopper-isonitrile complex (**4**), a copper carbenoid-isonitrile complex, which was then treated with an α,β-unsaturated carbonyl compound to produce the cyclopropane derivative **5** (eq 2). A reaction scheme involving conjugate addition and subsequent 1,3 elimination of copper halide was proposed.

Now, we find that employment of allylidene dichloride as the polyhalomethane component in the above reaction (eq 2) leads to the formation of vinyl-substituted cyclopropanes (**1**) in moderate yields. By heating a mixture of allylidene dichloride, diethyl fumarate, metallic copper, and an isonitrile in benzene at 80°, 1-vinyl-2,3-bis(ethoxycarbonyl)cyclopropane (67% yield) was produced, uncontaminated with stereoisomers, as judged by tlc. The reaction of allylidene dichloride with diethyl maleate produced the same vinylcyclopropane derivative. In addition, diethyl maleate and *cis*-1,2-bis(ethoxycarbonyl)cyclopropane were isomerized to the respective trans isomers by the copper–isonitrile system.[3] These findings may allow the assumption that the two ethoxycarbonyl groups on 1-vinyl-2,3-bis(ethoxycarbonyl)cyclopropane are oriented trans to each other. The nonequivalency of the two ethoxycarbonyl groups in the nmr spectrum is in accord with this assignment (see Experimental Section).



(2)

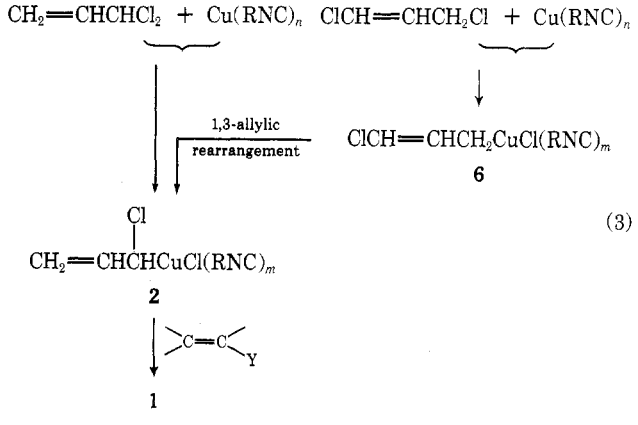
3 **4** **5**

X = Ph, CO_2R, CN
Y = CO_2R, CN

In a similar way, the reactions of *trans*-cinnamylidene dichloride with diethyl fumarate or with diethyl maleate gave a single product, 1-(*trans*-styryl)-2,3-bis(ethoxycarbonyl)cyclopropane, in 77 and 43% yield, respectively, in which the two ester groups were assigned to be trans to each other from the above reasoning. On the other hand, the reaction of *trans*-cinnamylidene dichloride with methyl acrylate afforded a mixture of *cis*- and *trans*-1-(*trans*-styryl)-2-methoxycarbonylcyclopropane in 66% yield.

The reaction with *trans*-crotylidene dichloride produced the corresponding (*trans*-propenyl)cyclopropane derivative only in poor yield, probably owing to the instability of crotylidene dichloride under the reaction conditions. These results are summarized in Table I. The reactions of allylidene dichloride with other electron-deficient olefins by this procedure, however, afforded the corresponding vinylcyclopropane only in low yields and selectivities.

It is noteworthy that the reaction of 1,3-dichloropropene with α,β-unsaturated carbo esters gave the same products in almost the same yields as with allylidene dichloride (Table I). This result may be taken to suggest a common reaction intermediate. We wish to propose the 1-chloro-2-propenylcopper isonitrile complex **2** as the common intermediate. Probably, 3-chloro-2-propenylcopper isonitrile complex **6** is initially formed in the reaction of 1,3-dichloropropene with the copper isonitrile complex and then rearranges to **2**. Rapid 1,3 rearrangement of allylic organometallic compounds is well known.[4] A probable reaction scheme is shown below (eq 3).



(3)

6 **2** **1**